Remarks

Claims 1-32 and 35-36 are now pending in this application. Claims 33 and 34 have been withdrawn from consideration and canceled. Claims 1, 26, 28, and 32 have been amended and new claims 35 and 36 have been added. The objections and rejections raised in the Office Action dated January 30, 2003 are addressed below. Applicants respectfully request reconsideration of the amended version of the claims in light of the following remarks.

Support for Amendments

The specification has been amended to correct minor grammatical errors and to include the serial number for an incorporated reference. The claims have been amended to further clarify the coating composition and radiation source. Support for the claim amendments is found, for example, on page 6, lines 1-4 and 21-29, of the present specification. No new matter is added by the amendments.

Election/Restrictions

Applicants hereby affirm the election to prosecute the invention of group I, claims 1-32, while preserving the right to pursue the non-elected claims in divisional applications.

Drawings

The drawings have been objected due to certain informalities. Applicants request clarification regarding the objection to the drawings. The Draftsperson's review indicates that color drawings are only acceptable if a petition is granted, but the drawings submitted in this case are black and white photographs. Three full-tone sets of the photographs are submitted herewith.

Specification

The specification has been objected to because the serial number of an incorporated reference is missing. Accordingly, Applicants have amended the specification to include the missing serial number. This objection may now be withdrawn.

§ 102 Rejections

Hanneman

Claims 1-3, 7-8, 14, 18, 20, 26, and 28 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Hanneman (U.S. Patent No. 4,327,155). The Office Action asserts that Hanneman discloses all of the elements recited in these claims. Applicants respectfully traverse this rejection as applied to the amended version of the claims.

A patent claim is anticipated only if each and every element as set forth in the claim is found in a single prior art reference. *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631 (Fed. Cir. 1987). Hanneman describes applying a coating on the surface of a substrate by plasma or flame spraying the surface with a powdered metal or a powdered metal oxide blend having an effective amount of a UV sensitive phosphor to produce a UV sensitive metallic or ceramic coating (col. 2, lines 13-21). The only coating materials described by Hanneman are inorganic compositions, either protective metal or ceramic coatings, that are applied to metal or ceramic substrates in order to prevent erosion or corrosion. In contrast, the amended claims of the present application recite a list of coating compositions that includes waxes, polymers, antimicrobial compositions, mildew growth preventing compositions, and other organic compositions, which are distinct from Hanneman's coating compositions. Hanneman fails to describe the use of any of the coating compositions listed in the amended claims. Hanneman, therefore, does not disclose all of the claim elements and thus does not anticipate the amended claims.

Applicants respectfully submit that the rejection of claims 1-3, 7-8, 14, 18, 20, 26, and 28 under 35 USC § 102(b) as being anticipated by Hanneman has been overcome and should be withdrawn.

Bumpus

Claims 1, 13, and 32 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Bumpus (U.S. Patent No. 5,023,019). The Office Action asserts that Bumpus discloses all of the elements recited in these claims. Applicants respectfully traverse this rejection as applied to the amended version of the claims.

Bumpus describes a flame- or fire-retardant composition that is formed as an aqueous solution of ammonium sulfate, sodium metasilicate, and an ammonium phosphate, such as

monoammonium phosphate (col. 4, lines 8-12). When applied to absorbent or cellulosic fibrous material, the ammonium sulfate, an inorganic salt, penetrates into the fibers to provide the treated article with fire- or flame-retardant properties, while the metasilicate salt serves as a binder (col. 4, lines 14-16). Monoammonium phosphate acts as an oxygen-starving agent to help prevent the spread of fire and flame on the treated article (col. 4, lines 21-23). Bumpus further discloses that the preparation may include a fluorescent agent as an additive to allow one to test the effectiveness of the treatment (col. 3, lines 55-59).

This preparation of inorganic salts is the only type of treatment composition described by Bumpus. The coating compositions recited in the amended claims are quite different from the Bumpus preparation. In particular, the amended claims recite a list of coating compositions that includes waxes, polymers, and other organic compositions. Bumpus does not describe the use of any of the coating compositions listed in the amended claims. Since Bumpus fails to disclose all of the claim elements, this reference does not anticipate the amended claims.

Applicants further note that, with respect to claims 1 and 13, which are directed to methods of detecting wear on a substrate, Bumpus does not teach detecting the presence or absence of fluorescence <u>after</u> the substrate has been exposed to wear, and thus does not describe a method for detecting wear. Rather, Bumpus describes using a fluorescent indicator as means for determining the <u>quality</u> of the treatment (col. 3, lines 55-59), for example, to determine whether the flame- or fire-retardant treatment was applied evenly and completely covered the desired areas of the treated article. Bumpus does not disclose that the presence or absence of fluorescence can serve as a means for determining wear. In fact, the Bumpus treatment is described as being "persistent and durable" and "does not lose its flame- or fire-retardant properties if the article is dry cleaned." (col. 3, lines 10-12). Bumpus' stated goal is to provide a treatment that "will not wear off and will withstand numerous washings." (col. 3, lines 7-15). Bumpus further reports that "this fire- or flame-retardant treatment has been found to be exceptionally durable and is not noticeably diminished, even by ten or more cycles of laundering or dry cleaning. The treatment is considered permanent." (col. 5, lines 40-45). Thus, although Bumpus may describe exposing a substrate to wear, Bumpus does not disclose that fluorescence should be used to detect the level of wear. On the contrary, since Bumpus teaches that the treatment is "permanent" and "will not wear off," there would be no reason to determine the level of wear.

In support of the Patent Office's assertion that Bumpus describes a method for detecting wear, the Office Action cites col. 5, lines 32-34, which discloses that the treatment "can be quickly checked at periodic intervals." However, nothing in this statement indicates that the substrate has been exposed to wear prior to being irradiated with UV light. Rather, as Bumpus explains in the preceding sentence, the inclusion of a fluorescent agent in the treatment preparation simply allows an inspector to later verify that the articles in question have, in fact, been treated and to determine the effectiveness of the treatment, i.e. the sufficiency of coverage, to make sure applicable fire code requirements have been satisfied (col. 5, lines 29-33). Bumpus describes the type of inspection that is contemplated after application of the flame- or fire-retardant preparation:

> For non-destructive inspection of articles <u>for testing both whether, and how well, they have been treated</u> the solution includes a fluorescent agent which emits visible light of a characteristic color when illuminated with long wave ultraviolet. (Col. 3, lines 55-59; emphasis added).

Nothing in this description, or elsewhere in the Bumpus reference, teaches or suggests that the fluorescent agent is used to determine the level of wear. This is hardly surprising given that Bumpus characterizes the treatment as "permanent."

In sum, since Bumpus fails to describe a coating composition of the type recited in the amended claims and also fails to describe a method of determining wear, Bumpus does not describe all of the elements of the amended claims. The rejection of claims 1, 13, and 32 under 35 USC § 102(b) as being anticipated by Bumpus has been overcome and should be withdrawn.

<u>§ 103 Rejections</u>

<u>Chauvette</u>

Claims 1, 4-6, 9-12, 16-17, 19, 22-24, and 28 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Chauvette et al. (U.S. Patent No. 6,391,226). Applicants respectfully traverse this rejection as applied to the amended version of the claims.

The Office Action asserts that Chauvette discloses a method for detecting wear on a substrate by coating the surface with a coating composition containing a fluorescent compound, exposing the coated surface to wear, having a means to activate the fluorescent compound, and detecting fluorescence (Office Action, p. 6). The Office Action acknowledges that Chauvette does not directly disclose that radiation is used to excite fluorescence in the coating, but asserts

that "it is very well known to use a radiation source to cause an item to fluoresce, and it would be obvious to one of ordinary skill at the time the invention was made to use a radiation source, such as an exciting light, in order to cause the fluorescent sensor in the coating to fluoresce." *Id.* Applicants respectfully disagree.

In order to establish a *prima facie* case of obviousness, the Patent Office must demonstrate that (1) there is a suggestion or motivation in the prior art to modify or combine reference teachings, (2) one skilled in the art would have had a reasonable expectation of success in making the modification or combination, and (3) the prior art reference(s) disclose all of the claim limitations. The fact that one of ordinary skill in the art would have had the capability to modify the method disclosed in the prior art reference(s) is not sufficient. MPEP 2143.01. The prior art reference(s) must provide a motivation or reason for making the changes. MPEP 2142; *Ex parte Chicago Rawhide Manufacturing Co.,* 226 USPQ 438 (PTO Bd. App. 1984).

Applicants submit that the presently claimed invention is not obvious in view of Chauvette, because there is no suggestion or motivation in Chauvette to use ultraviolet radiation to activate the sensors in the coating materials. Instead, Chauvette teaches that a chemical composition referred to as a "revealer" should be applied to the coating in order to activate the sensor (col. 4, lines 6-8). Chauvette explains that the revealer consists of "a formulation containing in an excipient, a compound <u>that will react with the sensor</u> to activate it (i.e. turn it colored)." (col. 4, lines 27-30; emphasis added). After the revealer has been applied and the coating has been inspected, an "eraser" composition is then applied to the coating in order to deactivate the sensor (col. 4, lines 12-14). According to Chauvette, the eraser "may consist of a formulation containing in an appropriate excipient, a compound that will react with the sensor to deactivate it (i.e. return it to its original color, normally to become colorless, transparent)." (col. 4, lines 31-35). Thus, Chauvette clearly teaches <u>chemical</u> activation and deactivation of the sensor, and does <u>not</u> teach or suggest using <u>radiation</u> to activate the sensor.

The preferred sensors cited in Chauvette, namely phenolphthalein, thymolphthalein, and ortho-cresolphthalein (col. 6, lines 25-35), are all commonly used as pH indicators (see, e.g., Exhibits A&B, attached hereto). These compounds are soluble in alcohol when in free base form (unionized) and the methanol or ethanol solutions are colorless with absorption maximum at a short UV wavelength range (200 - 300 nm); the excited molecules do not return to ground state

by emitting radiation, and thus they are not fluorescent dyes and no visible color will be observed under a black light irradiation.

These compounds are soluble in alkaline solution and the solution remains colorless when the pH of the solution is lower than their pKa value; however, when the pH of the solution is raised to above their pKa value and most of the molecules are in ionized form, the solution will turn a red, blue or pink color. Thus, the "revealer" composition described by Chauvette is essentially a high pH solution that is used to ionize the sensor and produce color. In this case, one would have no reason to use UV radiation (e.g., black light) to reveal the visible color.

As noted in the Office Action, Chauvette also identifies two fluorescent compounds, β-Naphthol and Coumarin, as potential sensors (col. 3, lines 40-42). These compounds are unionized at lower pH (<9). β-Naphthol does fluoresce with an absorption wavelength in the range of 200 to 400nm; however, the emission wavelength for this compound is between 300 to 400nm, which is still in the UV range not the visible range (approximately 400 to 750nm). (See Exhibit C, attached hereto, which reports emission at the fluorescence maximum of approximately 350nm.) Thus a spectrophotometer would likely be needed to effectively detect the emitted radiation. *Id.* If one were merely to shine a black light on the substrate surface, little or no visible color would be observed. Similarly, unsubstituted Coumarin is described in the literature as emitting little fluorescence (see Exhibit D, attached hereto).

Furthermore, when treated with a composition that raises the pH to above 10.5, which is precisely the kind of "revealer" composition described by Chauvette, β-Naphthnol would be in ionized form and would have very intense color in the visible light region. Under these circumstances, there would be no need to use black light to activate the compound since the activation (i.e., color change) is accomplished through a change in pH. In other words, as with phenolphthalein, thymolphthalein, and orthocresophthalein, β-Naphthnol can also be chemically activated by altering the pH conditions so as to become colored under visible light conditions, without being exposed to a source of ultraviolet radiation (e.g., black light). Thus, Chauvette's identification of these fluorescent compounds as potential sensors would not have motivated one skilled in the art to use UV radiation as means for producing color. On the contrary, since Chauvette teaches that the sensors should be activated by exposure to a chemical revealer (e.g. an alkaline solution) and since the fluorescent compounds identified by Chauvette have an emission wavelength outside the visible range, one skilled in the art would have been led away from using

UV radiation to activate the sensors. See *W.L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540 (Fed. Cir. 1983) (holding that obviousness determinations under § 103 require that the prior art references be considered as a whole, including portions that would lead away from the claimed invention.)

The passages of Chauvette cited in the Office Action cannot be read in a vacuum, and must be placed in their proper context. The portions of Chauvette that refer to the use of fluorescent sensors falls squarely within Chuavette's discussion of using chemical compositions as revealers. Since the Chauvette system centers on chemical activation of the sensor (e.g., by raising pH), indeed no other means for activation is disclosed, one skilled in the art would have been led to use a chemical means of activating the fluorescent sensors, rather than using UV radiation, especially in light of the fact that these compounds can be made to produce color by raising the pH of the solution, just as with the other pH indicators that Chauvette describes as preferred sensors. Moreover, one of ordinary skill would not have been motivated to use UV radiation (e.g., black light), because it would not have produced the desired effect, i.e. a visible color change, when used with the particular fluorescent compounds identified by Chauvette. In particular, a spectrometer would probably be needed to effectively detect the emitted light from β-Naphthol in view of its emission wavelength (see Exhibit C). Such a detection means would have been impracticable and inconsistent with Chauvette's stated purpose – providing a visual monitoring system that is very simple and allows for a reduction of the burden on the employees responsible for applying and maintaining floor finishing compositions (col. 2, lines 63-67). Since Chauvette lacks any teaching or suggestion to expose the coated substrate to UV radiation and provides no motivation to perform this step, this reference is not sufficient to establish a *prima facie* case of obviousness.

In view of the foregoing amendments and remarks, Applicants respectfully submit that the rejection of claims 1, 4-6, 9-12, 16-17, 19, 22-24, and 28 under 35 U.S.C. § 103(a) as being unpatentable over Chauvette has been overcome and should be withdrawn.

Hanneman

Claims 15, 25, 27, 30, and 31 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Hanneman (U.S. Patent No. 4,327,155.) Applicants respectfully traverse this rejection as applied to the amended version of the claims.

Claims 15, 25, and 27 depend directly or indirectly from claim 1. Claims 30 and 31 depend from claim 28. Each of these dependent claims adds a limitation to the claim from which it depends. Although, as acknowledged by the Examiner, Hanneman does not specifically disclose these additional limitations, the Office Action asserts that such features would be obvious.

For the reasons discussed above, claim 1 and claim 28 are patentable over Hanneman. Claims 15, 25, 27, 30, and 31 are likewise patentable over Hanneman for the same reasons since these claims all depend from claim 1 or 28. The rejection under § 103(a) should, therefore, be withdrawn.

Conclusion

In view of the foregoing amendments and remarks, Applicants respectfully submit that the application is in condition for allowance. Reconsideration of the application is requested.

A Request for Extension Of Time Under 37 CFR § 1.136(a) and authorization to charge the extension of time fee to Assignee's deposit account is included with this Amendment.

All communications in this case should be direct to the undersigned. If the Examiner believes a telephone discussion would be helpful to resolve any of the outstanding issue in this case, the Examiner is encouraged to call the undersigned at the number listed below.

Respectfully submitted,

May 30, 2003
Date

By: Sean Edman

Sean J. Edman, Reg. No.: 42,506
Telephone No.: 651-575-1796

Office of Intellectual Property Counsel
3M Innovative Properties Company
Facsimile No.: 651-736-3833

Version with markings to show amendments made:

In the Specification:

On page 1, the paragraph starting on line 24 and ending on line 2 of page 2 has been amended as follows:

In one aspect, the invention features a method of detecting wear on a substrate, the method including coating a composition that includes a fluorescent compound on the surface of a substrate, exposing the coated surface to wear, exposing the coated surface to radiation capable of exciting the fluorescent compound, and detecting the presence or absence of fluorescence. In one embodiment, the radiation includes ultraviolet light. In other embodiments, the radiation has a wavelength of from 200 nm to 400 nm. In one embodiment, the fluorescent compound emits visible light. In other embodiments, the fluorescent compound emits radiation having a wavelength of from 400 nm to 750 nm. In another embodiment, the detecting includes visually observing the presence or absence of fluorescence.

On page 2, the paragraph starting on line 21 and ending on line 30 has been amended as follows:

In some embodiments, the method further includes coating a second composition on the coated surface prior to exposing the coated surface to wear. In another embodiment, the method further includes coating a first layer and a second layer on the coated substrate after coating the substrate with the composition that includes a fluorescent compound. In other embodiments, the step of coating includes coating a portion of the substrate surface with the composition that includes a fluorescent compound. In one embodiment, the method further includes coating a first portion of the substrate surface with the composition that includes a fluorescent compound and coating a second portion of the substrate with a second composition, the second composition being essentially free of the fluorescent compound.

On page 3, the paragraph starting on line 21 and ending on line 29 has been amended as follows:

In other aspects, the invention features a method of determining the degree of wear on a coated surface of a substrate, the surface having previously been coated with a composition that includes a fluorescent compound, the method includes exposing the coated substrate to radiation capable of exciting a the fluorescent compound, measuring the fluorescence intensity emitted from the coated surface, and comparing the measured fluorescence intensity with a predetermined fluorescence intensity. In one embodiment, the predetermined fluorescence intensity includes a calibration curve. In other embodiments, the predetermined fluorescence intensity includes a fluorescence intensity value previously obtained from the coated substrate.

On page 3, the paragraph starting on line 30 and ending on line 4 of page 4 has been amended as follows:

In some aspects, the invention features a method of detecting coverage of a coating on a substrate, the method includes, coating a substrate with a composition that includes a fluorescent dye essentially free of organosilicone, affixing the composition to the substrate, exposing the coated substrate to radiation capable of exciting the fluorescent dye, and detecting the presence or absence of fluorescence across the coated surface to determine the extent of surface coverage by the coating composition.

On pages 6-7, the paragraph starting on line 30 of page 6 and ending on line 9 of page 7 has been amended as follows:

One example of a useful aqueous composition includes fluorescent compound, silane (for example, n-alkylalkoxysilane, condensates n-alkylalkoxysilane or a combination thereof), cationic quaternary ammonium surfactant and water. The composition preferably also includes siloxane (for example, methyl hydrogen siloxane methylhydrogen-methylalkyl siloxane copolymers (for example, methylhydrogen-dimethyl siloxane copolymers), methylhydrogen-cyclosiloxane copolymers and methylhydrogen-methylalkyl cyclosiloxane copolymers) and

volatile carrier, that is, a carrier capable of volatilizing at room temperature after application on a substrate. Such compositions are disclosed in U.S. Patent Application Serial No. [____________] 10/001,079, entitled, “Stain Resistant Treatment For Porous Substrates” filed October 30, 2001, Attorney Docket No. 57133US002 and incorporated herein.

In the Claims:

Claims 1, 26, 28, and 32 have been amended as follows:

1. A method of detecting wear on a substrate, said method comprising:

a. coating a composition comprising a fluorescent compound on the surface of a substrate, wherein said composition is selected from waxes, floor finishing compositions, sealants, polishing compositions, antimicrobial compositions, water proofing compositions, antigraffiti compositions, antisoiling compositions, mildew growth preventing compositions, water repellent compositions, antislipping compositions, and polymer compositions;

b. exposing the coated surface to wear;

c. exposing the coated surface to ultraviolet radiation capable of exciting the fluorescent compound; and

e. detecting the presence or absence of fluorescence.

26. A method of detecting wear on a substrate surface, said method comprising:

a. providing a substrate that has been previously coated with a composition comprising a fluorescent compound, the coated surface having been exposed to wear, wherein said coating composition is selected from waxes, floor finishing compositions, sealants, polishing compositions, antimicrobial compositions, water proofing compositions, antigraffiti compositions, antisoiling compositions, mildew growth preventing compositions, water repellent compositions, antislipping compositions, and polymer compositions; [said method comprising:]

[a]b. exposing the surface to ultraviolet radiation capable of exciting the fluorescent compound; and

[b]c. detecting the presence or absence of fluorescence.

28. A method of determining the degree of wear on a coated surface of a substrate, said method comprising:

a. providing a substrate [said] surface having previously been coated with a composition comprising a fluorescent compound, wherein said coating composition is selected from waxes, floor finishing compositions, sealants, polishing compositions, antimicrobial compositions, water proofing compositions, antigraffiti compositions, antisoiling compositions, mildew growth preventing compositions, water repellent compositions, antislipping compositions, and polymer compositions; [said method comprising:]

[a]b. exposing the coated substrate to ultraviolet radiation capable of exciting the fluorescent compound;

[b]c. measuring the fluorescence intensity emitted from said coated surface; and

[c]d. comparing the measured fluorescence intensity with a predetermined fluorescence intensity.

32. A method of detecting coverage of a coating on a substrate, said method comprising:

a. coating a substrate with a composition comprising a fluorescent dye, wherein said coating composition is selected from waxes, floor finishing compositions, sealants, polishing compositions, antimicrobial compositions, water proofing compositions, antigraffiti compositions, antisoiling compositions, mildew growth preventing compositions, water repellent compositions, antislipping compositions, and polymer compositions [essentially free of organosilicone];

b. affixing said composition to said substrate;

c. exposing the coated substrate to ultraviolet radiation capable of exciting the fluorescent dye; and

d. detecting the presence or absence of fluorescence across the coated surface to determine the extent of surface coverage by the coating composition.

EXHIBIT A

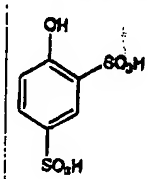
Guide to Chemical Hazards (DHHS/NIOSH 90-117, 1990) p 176; *Clinical Toxicology of Commercial Products*, R. E. Gosselin *et al.*, Eds. (Williams & Wilkins, Baltimore, 5th ed., 1984) Section III, p 344-348; *Patty's Industrial Hygiene and Toxicology* vol. 2A, G. D. Clayton, F. E. Clayton, Eds. (Wiley-Interscience, New York, 3rd ed., 1981) p 2567-2584.

USE: As a general disinfectant, either in soln or mixed with slaked lime, etc., for toilets, stables, cesspools, floors, drains, etc.; for the manuf of colorless or light-colored artificial resins, many medical and industrial organic compds and dyes; as a reagent in chemical analysis. Pharmaceutic aid (preservative).

THERAP CAT: Aqueous soln as topical anesthetic; topical antiseptic; topical antipruritic.

THERAP CAT (VET): Antiseptic caustic. Topical anesthetic in pruritic skin conditions. Has been used internally and externally as an antiseptic.

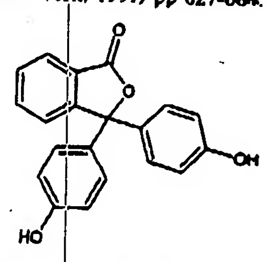
7391. Phenoldisulfonic Acid. *4-Hydroxy-1,3-benzenedisulfonic acid; 4-hydroxy-m-benzenedisulfonic acid;* 1-phenol-2,4-disulfonic acid. $C_6H_6O_7S_2$; mol wt 254.24. C 28.35%, H 2.38%, O 44.05%, S 25.22%. Conveniently prepd by hydrolysis of the dichloride which is obtained by the action of chlorosulfonic acid on phenol at room temp: Pollak *et al.*, *Monatsh.* **46**, 395 (1925). Monograph: E. E. Gilbert, *Sulfonation and Related Reactions* (Interscience, New York, 1965) 529 pp.



Deliquescent needles, vague melting range from 89° to 100°. Decomp above 100°. Freely sol in water, methanol. Practically insol in ether, petr ether.

USE: In the manuf of aminophenoldisulfonic acids which are intermediates in the dye industry.

7392. Phenolphthalein. *3,3-Bis(4-hydroxyphenyl)-1(3H)-isobenzofuranone;* 3,3-bis(*p*-hydroxyphenyl)phthalide; α-(*p*-hydroxyphenyl)-α-(4-oxo-2,5-cyclohexadien-1-ylidine)-*o*-toluic acid; Chocolax; Darmol. $C_{20}H_{14}O_4$; mol wt 318.33. C 75.46%, H 4.43%, O 20.10%. Prepd by condensing phenol with phthalic anhydride: Baeyer, *Ann.* **202**, 69 (1880); Herzog, *Chem. Ztg.* **51**, 84 (1927); Hubacher, U.S. pat. 2,192,485 (1940 to Ex Lax); Gamrath, U.S. pat. 2,522,939 (1950 to Monsanto). Subchronic toxicity studies: D. D. Dietz *et al.*, *Fund. Appl. Toxicol.* **18**, 48 (1992). Comprehensive description: F. J. Al-Shammary *et al.* in *Analytical Profiles of Drug Substances* vol. 20, K. Florey Ed. (Academic Press, New York, 1991) pp 627-664.



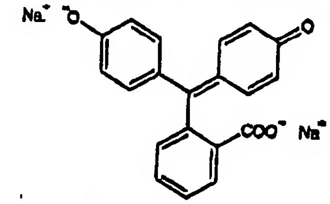
Minute, triclinic crystals, often twinned. mp 258-262°. d 1.299. Color: White or yellowish-white, *see also* Yellow Phenolphthalein. Sol in alcohol and ether, very slightly sol in chloroform. One gram dissolves in 12 ml alcohol, in ~100 ml ether. Almost insol in water. Sol in dil solns of alkali hydroxides and hot solns of alkali carbonates forming a red soln. pKa (25°C) 9.7. uv max (methanol): 205, 229, 276 nm (ε 27261.147, 14692.144, 2006.369).

USE: A 1% alcoholic soln as an indicator in titrations of mineral and organic acids and most alkalies. Not suitable for ammonia. Very sensitive to CO_2, and in estim[ating] carbonates the liq must be boiled. Borax can be dete[rmined] with phenolphthalein as an indicator only when glycer[ol is] present, because the color gradually fades away as the [...] is added. Usable with a few alkaloids. Colorless to pH [...] pink to deep-red, > pH 9.

THERAP CAT: Cathartic.

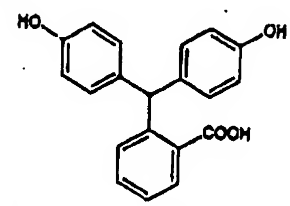
THERAP CAT (VET): Has been used as a laxative.

7393. Phenolphthalein Sodium. *3,3-Bis(4-hyd[roxy]phenyl)-1(3H)-isobenzofuranone disodium salt.* $C_{20}H_{[12]}$ O_4 [...] mol wt 362.29. C 66.31%, H 3.34%, Na 12.6[9]%, [O] 17.66%. Prepd from an alcoholic soln of 1 mol phe[nol]phthalein by the addition of 2 mols NaOH. Structu[re:] Buu-Hoi, *Bull. Soc. Chim.* [5] **8**, 165 (1941).



Reddish-brown granular mass with coppery lust[er or] pale red powder. Dec in air. Soluble in water, giving [a] deep-red soln. Absorption max: 550-555 nm. The unstab[le] enol form is colorless, as is the trisodium salt.

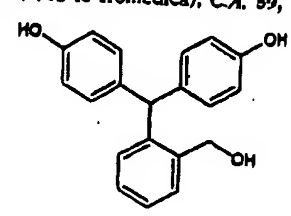
7394. Phenolphthalin. *2-[Bis(4-hydroxyphenyl)methyl]benzoic acid;* decolorized phenolphthalein; phthalin; 4',4''-dihydroxytriphenylmethane-2-carboxylic acid. $C_{20}H_{16}O_4$; mol wt 320.34. C 74.99%, H 5.03%, O 19.98%. Made b[y] boiling phenolphthalein with zinc dust in alkaline sol[n]. Called *"Kastle-Meyer reagent"* when in soln. Prepd by dis[solving] 2 g phenolphthalin + 20 g KOH in a desired amt of doubly distd H_2O and diluting with an equal vol of 9[5%] ethanol. Detailed directions for prepn of test soln and [...] use: Lecoq, *Bull. Soc. Chim. Belge* **54**, 186-202 (1945), *C.A.* **41**, 2346i (1947).



Colorless crystals, mp 237°. Insol in water; sol in alcohol, ether, aq alkali. The alkaline solns gradually become pink on exposure to air or other oxidizing substances.

USE: As a reagent for oxidases, blood, HCN, peroxides, copper.

7395. Phenolphthalol. *2-[Bis(4-hydroxyphenyl)methyl]benzenemethanol; o-[bis(p-hydroxyphenyl)methyl]benzyl alcohol;* dihydroxyphenylmethenylbenzyl alcohol; 2-(4,4'-dihydroxybenzhydryl)benzyl alcohol; bis(4-hydroxyphenyl)(2-hydroxymethylphenyl)methane; Egmol; Regolax. $C_{20}H_{18}O_3$; mol wt 306.36. C 78.41%, H 5.92%, O 15.67%. Prepn: Hubacher, *J. Am. Chem. Soc.* **74**, 5216 (1952); Schultz, Geller, *Arch. Pharm.* **288**, 234 (1955); Bulesu, Ger. pat. 1,141,293 (1962 to Iromedica), *C.A.* **59**, 1535b (1963).



Crystals from dil alcohol, mp 201-202°.

Monoacetate, [...] form, mp 171-17[...]
Triacetate, C[...] mp 104-106°. [...]
THERAP CAT: C[...]

7396. *p*-Phe[...] *ic acid;* sulfocar[...] 41.38%, H 3.47%, [...] able as a 65% sol[...] bromobenzenesul[...] 1,321,271 (1920) [...] Byrne, Brit. pat. [...] Prepn of ammoni[...] 303.

Deliquescent n[...]
Ammonium sa[...] *nate.* Plates from [...]
Barium salt, [...] Monohydrate, po[...] in alcohol.
Caution: Irrita[...]
USE: Intermed[...] in the Ferrostan [...]

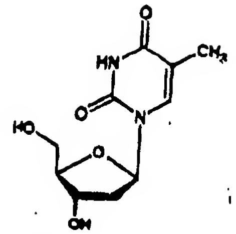
7397. Pheno[...] *ol-3-ylidene)bisph[...] oxyphenyl)-o-tolu[...] oxyphenyl)-3H-2[...]* P.S.P.; Sulfonphth[...] H 3.98%, O 22.5[...] fobenzoic anhydr[...] nol: Kekulé, Bar[...] 943 (1873); Heun[...] pat. 142,116; Ch[...] wood, *J. Am. Ch[...]* G. Dunca, P. F[...] (1968); R. D. Wil[...] 289 (1981).

Bright red to d[...] One gram dissolv[...] 500 ml acetone. [...] sol in aq alkali [...] which is discharg[...]
USE: As indic[...] yellow, 8.4 red.
THERAP CAT: D[...]
THERAP CAT (VE[...]

7398. Pheno[...] *3,3-bis(4-hydrox[...] tetrachlorophenol[...]* 32.67%, H 2.21% [...] sation of phenol [...] dride: W. R. Or[...] (1909); Zalkind, [...] 1210 (1935). M[...]

Consult the Name Index before using this section.

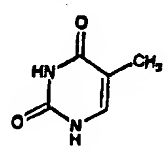
EXHIBIT B



Rosettes of needles from ethyl acetate. mp 185°. Yields a sublimate of thymine when heated. $[\alpha]_D^{25}$ +30.6° (c = 1.029). uv max (pH 7.2): 206.5, 267 nm ($\epsilon \times 10^{-3}$ 9.8, 9.7), Voet *et al., Biopolymers* **1**, 193 (1963). Sol in water, methanol, hot alcohol, hot acetone, hot ethyl acetate, pyridine, glacial acetic acid; sparingly sol in hot chloroform.

Monotrityl thymidine. $C_{29}H_{28}N_2O_5$, prepd by the action of triphenylmethyl chloride on thymidine in pyridine. mp 125°. $[\alpha]_D^{26}$ +11.4° (c = 1.01 in acetone).

9539. Thymine. *5-Methyl-2,4(1H,3H)-pyrimidinedione;* 5-methyluracil; 2,4-dihydroxy-5-methylpyrimidine. $C_5H_6N_2O_2$; mol wt 126.11. C 47.62%, H 4.80%, N 22.21%, O 25.37%. A pyrimidine derivative; constituent of nucleic acids. Originally isolated from thymus nucleic acid: Levene, *Z. Physiol. Chem.* **39**, 4 (1903). Prepn by heating 2-ethylmercapto-4-hydroxy-5-methylpyrimidine: Wheeler, Merriam, *Am. Chem. J.* **29**, 478 (1903); **43**, 29 (1910). From methylcyanacetylurea by catalytic reduction: Bergmann, Johnson, *J. Am. Chem. Soc.* **55**, 1733 (1933). From β-methylmalic acid: Scherp, *J. Am. Chem. Soc.* **68**, 912 (1946). Crystal structure of monohydrate: Gerdil, *Acta Cryst.* **14**, 333 (1961). *Review:* Ts'o, "Bases, Nucleosides and Nucleotides" in *Basic Principles in Nucleic Acid Chemistry* vol. 1, P. O. P. Ts'o, Ed. (Academic Press, New York, 1974) pp 453-584. *See also* Nucleic Acids.

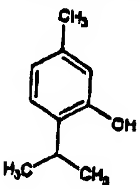


Dendritic or star-shaped plates from water, sometimes short needles. Sublimes in platelets. Dec 335-337° (Kofler stage). Weak acid, pK at 25° = 9.94. uv max (pH 7.0): 205, 264.5 nm ($\epsilon \times 10^{-3}$ 9.5, 7.9). Sol in hot water; slightly sol in cold water (4 g/l at 25°). Somewhat sol in alc; sparingly sol in ether; readily sol in alkalies with formation of salts. Oxidation yields urea, ethanal, pyruvic acid, formic acid. Hydrazine reacts with thymine forming urea and 4-methylpyrazolone. Thymine forms a silver salt which is sol in excess ammonia. Its mercuric and lead salts are insol.

Thymine-2-desoxyriboside, *see* Thymidine.

USE: In biochemical research.

9540. Thymol. *5-Methyl-2-(1-methylethyl)phenol;* 5-methyl-2-isopropyl-1-phenol; 1-methyl-3-hydroxy-4-isopropylbenzene; 3-*p*-cymenol; 3-hydroxy-*p*-cymene; thyme camphor; *m*-thymol. $C_{10}H_{14}O$; mol wt 150.22. C 79.96%, H 9.39%, O 10.65%. Isolated by Neumann in 1719. Obtained from the essential oil of *Thymus vulgaris* L. and *Monarda punctata* L., *Labiatae:* Arppe, *Ann.* **58**, 41 (1846); Meyer, *Pharm. Ztg.* **81**, 192, 205 (1936). Also occurs in other volatile oils. Produced synthetically from *p*-cymene, piperitone, or *m*-cresol: Austerwell, Brit. pat. 221,227 (1923); Jennen, Verdroncken, *Compt. Rend.* **245**, 183 (1957); Bottoms, U.S. pat. 2,840,615 (1958 to Natl. Cylinder Gas). Bactericidal activity: J. M. Schaffer, F. W. Tilley, *J. Bacteriol.* **14**, 259 (1927). Mold elimination on surfaces: O. W. Richards, K. J. Hawley, *J. Chem. Ed.* **16**, 6 (1939). In vitro antifungal activity: H. B. Myers, *J. Am. Med. Assoc.* **89**, 1834 (1927). Effectiveness as antifungal preservative: M. Dersarkissian, M. Goodberry: *Studies Conserv.* **25**, 28 (1980). Use as clinical preservative: T. Z. Liu, *Clin. Chem.* **25**, 336 (1979); T. Z. Liu *et al., ibid.* **27**, 1144 (1981). Toxicity: P. M. ... *et al., Food Cosmet. Toxicol.* **2**, 327 (1964).



Crystals, mp 51.5°. bp ~233°. Appreciably vola... 100°; volatilizes in water vapors. Characteristic odor, pungent, somewhat caustic taste. d_4^{25} 0.9699. n_D^{20} 1.522... 1.5204. One gram dissolves in ~1000 ml water, 1 ml alcohol, 0.7 ml chloroform, 1.5 ml ether, 1.7 ml olive oil... Sol in glacial acetic acid, oils, fixed alkali hydroxides... orally in rats: 980 mg/kg (Jenner).

Incompat: Acetanilide, antipyrine, camphor, monobromated camphor, chloral hydrate, menthol, quinine ..., salol, urethane, spirit nitrous ether; in triturations ... of liquefaction.

Acetate, $C_{12}H_{16}O_2$, *acetylthymol, thymyl acetate.* ...ish, oily liq; thymol odor. d^{0} 1.009. bp 243.5-245.5°... tically insol in water. Miscible with alcohol, benzene, chloroform, ether.

Caution: Mild irritant.

Carbonate, $C_{21}H_{26}O_3$, white crystals; thymol odor; ...izes with steam. mp 49°. Insol in water, acids, alkalies... in hot alcohol, chloroform, ether, carbon tetrachloride...

USE: For destroying mold; preserving documents, ... jects and urine. Stabilizer (antioxidant) for trichloro...ene, halothane.

THERAP CAT: Antiseptic (topical); anthelmintic (Nematodes).

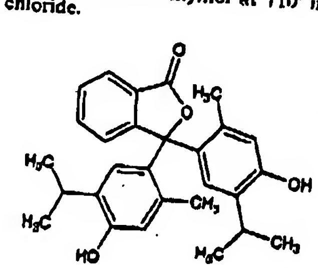
THERAP CAT (VET): Has been used as anthelmintic, ... an antiseptic, external and internal.

9541. Thymol Blue. *4,4'-(3H-2,1-Benzoxathiol-3-ylidene)bis[5-methyl-2-(1-methylethyl)phenol] S,S-dioxide; ... hydroxy-α,α-bis(5-hydroxycarvacryl)-o-toluenesulfonic ... γ-sultone;* thymolsulfonephthalein. $C_{27}H_{30}O_5S$; mol wt 466.60. C 69.50%, H 6.48%, O 17.14%, S 6.87%.

Brownish-green, cryst powder; characteristic odor. ... in water. Sol in alcohol, dil alkali solns.

USE: As an acid-base indicator; pH: red 1.2 to yellow ... also yellow 8.0 to blue 9.6.

9542. Thymolphthalein. *3,3-Bis[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]-1(3H)-isobenzofuranone; 5',5''-diisopropyl-2',2''-dimethylphenolphthalein.* $C_{28}H_{30}O_4$; mol wt 430.54. C 78.11%, H 7.02%, O 14.86%. Obtained by ...ing phthalic anhydride with thymol at 110° in the presence of stannic chloride.



Needles, mp ~253°. Insol in water; sol in alcohol, ...tone; also sol in dil alkalies with a blue color, in H_2SO_4 ... a carmine-red color.

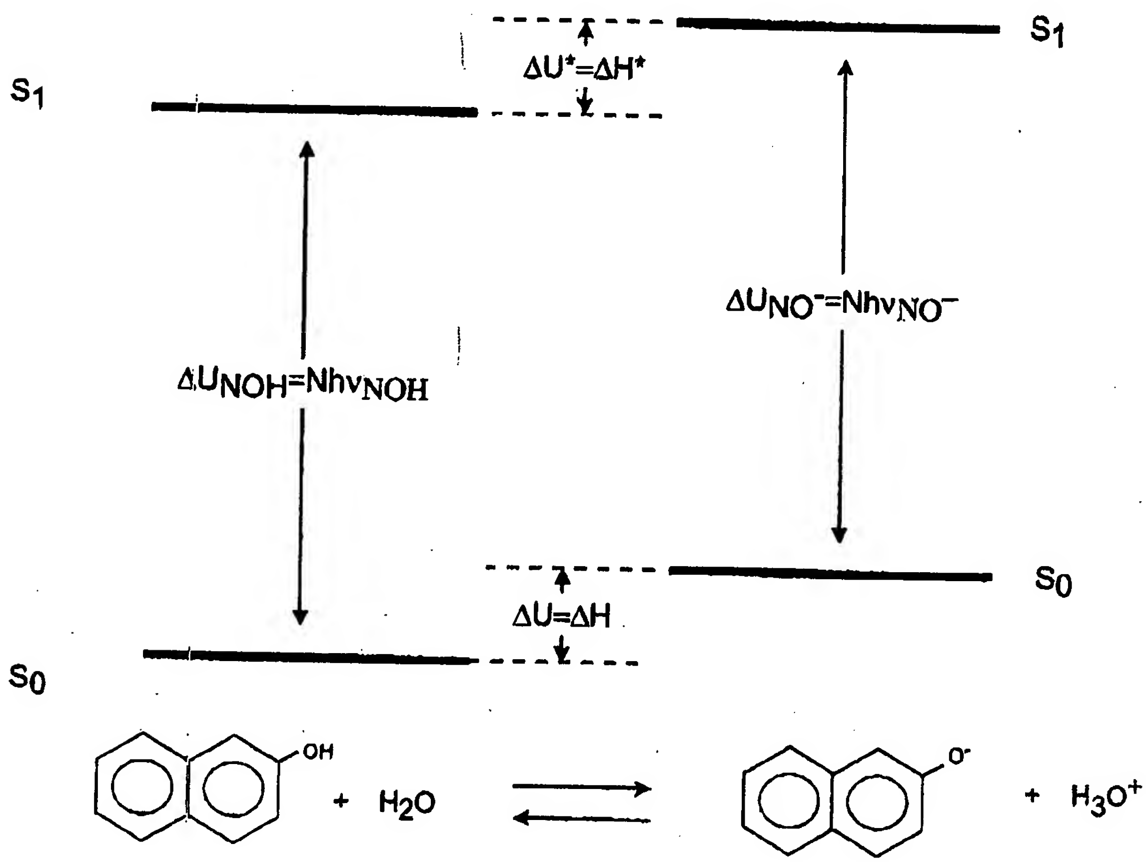
USE: As pH indicator: colorless 9.3 to blue 10.5. Also ... reagent for blood after decolorizing the alkaline soln ... boiling with zinc dust.

9543. Thymomodulin. Leucotrofina. Cell-free thy... hormone preparation extracted from calf thymus by ... hydrolysis. Composed of a mixture of biologically ... acidic peptides of mol wt < 10,000. Modulates the mat... tion of T-cells. Prepn of crude extract from calf thymus ...

EXHIBIT C

Excited State Properties of 2-Naphthol
Physical Chemistry Laboratory
Maria A. Gomez

The distribution of electrons around a molecule determines many of its properties. In this experiment, we will study how the proton dissociation properties of 2-naphthol change when light is used to change the distribution of electrons in the molecule. When 2-naphthol is in solution, it can lose a proton to a nearby water molecule. The equilibrium constant for this dissociation depends on whether 2-naphthol is in the ground or the first excited state. Consider the following diagram:



At the bottom of the diagram you see the equilibrium reaction that we are considering. 2-Naphthol is in equilibrium with its base form in water. The same is true in the excited state. However, the relative energy between the base and the acid form is different in the ground and first excited states. As a result, the equilibrium constant is different in

the ground and first excited state. The first week of this experiment you will find the equilibrium constant for this reaction in the ground and first excited state. During the second week, you will find the protonation and deprotonation rates for the first excited state. In addition, you will explore the HOMO and LUMO of 2-naphthol to understand what causes the different behavior in the ground and first excited states.

Ground and Excited State Equilibrium constants

Ground State Equilibrium Constant: To obtain the ground state equilibrium constant for this acid dissociation, it is useful to rearrange the definition of the equilibrium constant,

$$K_a = \frac{[H_3O^+][NO^-]}{[NOH]}.$$

In particular, take its log and rearrange the terms to obtain,

$$pH = pK_a + \log\frac{[NO^-]}{[NOH]} \text{ where } pK_a = -\log K_a \text{ and } pH = -\log[H_3O^+].$$

Using absorption spectroscopy, you will determine the concentrations of 2-naphthol and its conjugate base. The pH will be determined from a pH meter reading. Plotting pH versus $\log\frac{[NO^-]}{[NOH]}$ should yield a straight line with an intercept of the pKa.

Excited State Equilibrium Constant: To obtain the relationship between the ground and first excited state equilibrium constant, consider the energy level diagram. Notice that

$$\Delta U_{NOH} + \Delta U^* = \Delta U_{NO^-} + \Delta U.$$

ΔU_{NOH} in units of per mole is the energy of the photon needed to promote one molecule of 2-naphthol from the ground to the excited state times Avogadro's number. ΔU_{NO^-} is the energy of the photon needed to promote one molecule of the conjugate base from the ground to the excited state times Avogadro's number. The molar energy difference between protonated and unprotonated 2-naphthol in solution is ΔU for the system undergoing the deprotonation. $\Delta U \approx \Delta H$ since $\Delta(PV)$ is about zero for our liquid system. As a result,

$$N_A h\nu_{NOH} + \Delta H^* = N_A h\nu_{NO^-} + \Delta H.$$

Rearranging and making the approximation that the entropy difference between the protonated and unprotonated forms of 2-naphthol is the same in the ground and the excited state, we obtain

$$N_A h(\nu_{NO^-} - \nu_{NOH}) = \Delta H^* - \Delta H = \Delta G^* - \Delta G = -RT\ln K_a^* + RT\ln K_a$$

The last equality assumes we are working at standard conditions. Re-arranging this equation yields

$$-\ln K_a + \frac{N_A h(\nu_{NOH} - \nu_{NO^-})}{RT} = -\ln K_a^* .$$

Converting from natural log to base 10 logs and dividing by 2.303,[1]

$$pK_a^* = pK_a - \frac{N_A hc(\tilde{\nu}_{NOH} - \tilde{\nu}_{NO^-})}{2.303RT}.$$

In this equation, $\tilde{\nu}$ is in units of wavenumbers (/cm). Be sure to put in the speed of light in units of cm/s.

Once we have the equilibrium constant for the ground state, we can use it to find the equilibrium constant for the excited state. The only other pieces of information that we need are the frequency of light that takes the ground 2-naphthol molecule to its excited state and the frequency of light that takes the ground conjugate base molecule to its excited state.

There are a variety of ways to obtain the frequency of light needed to excite a molecule from it's ground state to the first excited state.
(i) Use the frequency at the absorption maximum.
(ii) Use the frequency at the fluorescence maximum of each species.
(iii) Use the 0-0 energy of the molecule. This is the frequency at which emission and excitation spectra cross.

During the first week of this lab you will obtain the data needed for all of these methods. In your report, you should describe the differences.

Excited State Protonation and Deprotonation Constants

---

[1] Here's how you convert from natural log to base 10 logs. Consider y=ln(x). This means that x=exp(y). Take the base 10 log of both sides of the equation. $\log(x) = \log(e^y) = y\log(e)$. Solving for y which is ln(x), we get $y = \ln(x) = \frac{\log(x)}{\log(e)} \approx 2.303\log(x)$.

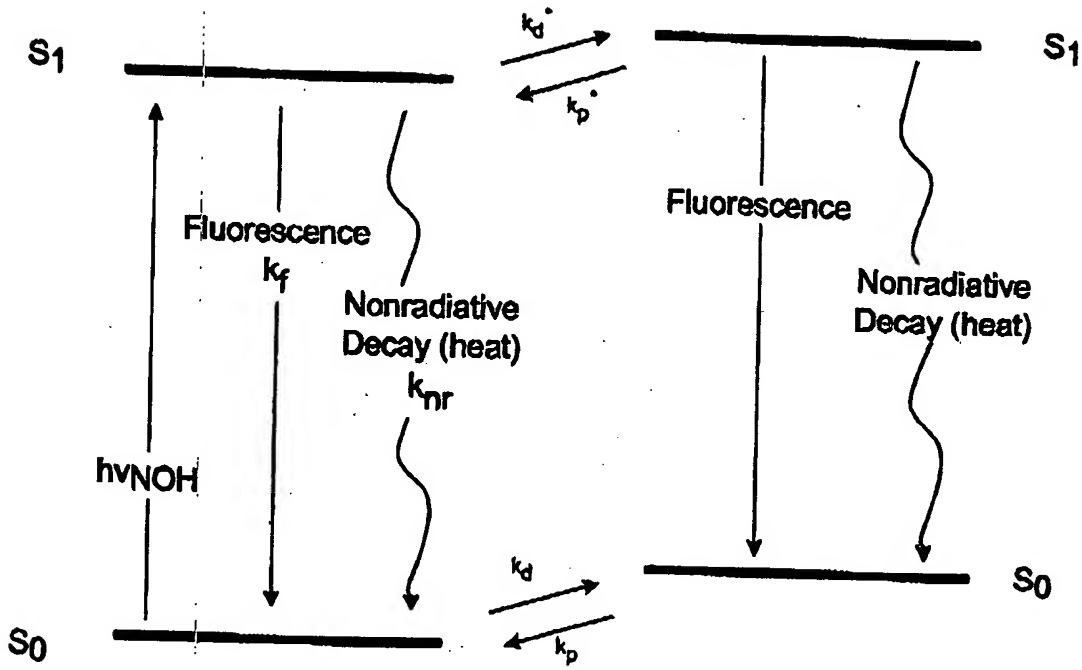
$$NOH + H_2O \underset{k_p}{\overset{k_d}{\rightleftarrows}} NO^- + H_3O^+ \qquad K_a = \frac{[H_3O^+][NO^-]}{[NOH]}$$

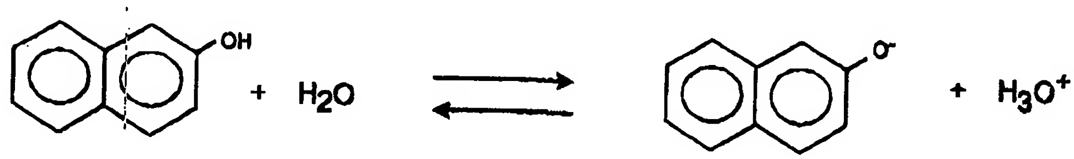
Now, we will obtain the rate of deprotonation and protonation in the excited state i.e. the forward and backward rates of the above reaction in the excited state. Notice that the pKa=-log Ka can be rearranged to yield the following relation:

$$\log\frac{[NOH]}{[NO^-]} = pK_a - pH.$$

From this rearrangement, it's clear that if the pH is lower than the pKa, the 2-naphthol predominates. However, when the pH is higher than the pKa, the conjugate base dominates. From the first part of this experiment, you will find out that 2-naphthol is a stronger acid in its excited state i.e. it's dissociation constant is larger in the excited state. The literature values for the ground and excited state acid equilibrium constants are 3.1×10^{-10} and 2.0×10^{-3}. As a result, the pKa is much lower in the excited state. This makes it possible to design an experiment in which the pH is lower than the ground state pKa but higher than the excited state pKa*. In such an experiment, 2-naphthol would predominate in the ground state. Then, it would be excited with light. In the excited state, 2-naphthol would quickly dissociate into its excited conjugate base. The excited conjugate base would decay to the ground state. It is also possible to design an experiment with the pH is lower than both of the pkas. In such a case, 2-naphthol would predominate in the ground and the excited state.

The beauty of playing with the pH of the solution is that we can change the pathway by which 2-naphthol decays back to the ground state. Consider the diagram below. Once 2-naphthol is excited, it can deprotonate or decay back to the ground state via either fluorescence or nonradiative decay. The plan is to first consider a solution with pH much lower than both the ground and excited state pKa i.e. a solution in which excited 2-naphthol can only get back to the ground state by fluorescing or nonradiative decay. In other words, the deprotonation route is blocked. This experiment would let us extract the sum of the rate constants for fluorescence and nonradiative decay. Once we have this sum, we could consider another experiment with a pH higher than pKa* but lower than pKa. In this experiment the deprotonation channel for excited 2-naphthol is open. With the data from such an experiment and the sum of the fluorescence and nonradiative decay rate constants, we'll be able to extract the deprotonation rate constant. The protonation rate constant is then obtained by dividing the deprotonation rate constant by the Ka*.





Here is a more concrete explanation of the strategy:

1. *Extracting the sum of the fluorescence and nonradiative decay rate constants:* Excite 2-naphthol in a solution with pH much lower than pKa and pKa*. Monitor the intensity of the light emitted by 2-naphthol. We don't have a fluorimeter capable of monitoring this so you will be provided with some data to analyze. The rate of depletion of excited 2-naphthol is

$$\frac{d[NOH^*]}{dt} = -(k_f + k_{nr})[NOH^*].$$

Separating concentration and time variables and integrating t from 0 to t and [NOH*] from $[NOH^*]_0$ to [NOH*].

$$\ln\frac{[NOH^*]}{[NOH^*]_0} = -(k_f + k_{nr})t$$

Since the fluorescence intensity is proportional to the concentration, we can replace $\frac{[NOH^*]}{[NOH^*]_0}$ by I/Io.

$$\ln\frac{I}{I_0} = -(k_f + k_{nr})t$$

You can plot ln(I/Io) versus time and obtain the sum of the fluorescence and nonradiative decay rate constants from the slope.

2. *Extracting the deprotonation constant:*

Now, we will consider a solution with pH lower than the pKa but higher than pKa*. We will obtain this pH by using an acetate buffer. Because acetate is being used, we actually add yet another channel for depletion of excited 2-naphthol. Now, there is a possible acetate assisted deprotonation. We will still be able to extract the deprotonation constant by varying the acetate concentration.

The analysis is made simpler by considering the concept of quantum yield. The quantum yield of 2-naphthol in a low pH solution is the fraction of 2-naphthol molecules that fluoresce down to the ground state.

$$\phi_0 = \frac{\text{rate of fluorescence}}{\text{rate of all decay to ground state}} = \frac{k_f[NOH^*]}{k_f[NOH^*] + k_{nr}[NOH^*]} = \frac{k_f}{k_f + k_{nr}}.$$

The quantum yield in the acetate solutions has two more terms in the denominator - a deprotonation rate and an acetate assisted deprotonation rate.

$$\phi = \frac{k_f^*}{k_f + k_{nr} + k_d^* + k_{Ac}^*[Ac^-]}$$

Notice that the acetate assisted deprotonation depends not only on the concentration of excited 2-naphthol but also the concentration of the acetate ion.

The ratio of these two quantum yields is proportional to the ratio of the fluorescence intensities and is equal to

$$\frac{\phi_0}{\phi} = \frac{I_0}{I} = 1 + \frac{k_d^*}{k_f + k_{nr}} + \frac{k_{Ac}^*}{k_f + k_{nr}}[Ac^-].$$

We will measure all the fluorescence intensities at the same wavelength. Clearly, from a plot of Io/I versus acetate concentration, we can obtain the deprotonation constant from the intercept and the sum of the fluorescence and nonradiative decay constants. Finally, we will obtain the protonation constant from its relationship with the acid equilibrium constant and the deprotonation rate constant.

$$K_a^* = \frac{k_d^*}{k_p^*}$$

The literature value for k_d^* is 6.0×10^7 /s. The literature value for $k_{Ac^-}^*$ is 2.3×10^9 L/mole/s.

Procedure:

A. pKas

(i) Preparing Solutions: Make a pure acid, a pure base, and some intermediate solutions as suggested in the table below. Prepare these in 50.0 mL volumetrics. Be sure you record as many decimal places as your measuring device allows. Measure the pH of the buffered solutions.

Solution	1.00X10-3 M 2-naphthol	1.00 M NH3	1.00 M NH4Cl	0.10 M H2SO4	0.10 M NaOH
pure acid	10.0 mL	0 mL	0 mL	10.0 mL	0 mL
pure base	10.0 mL	0 mL	0 mL	0 mL	10.0 mL
1	10.0 mL	5.0 mL	5.0 mL	0 mL	0 mL
2	10.0 mL	10.0 mL	5.0 mL	0 mL	0 mL
3	10.0 mL	5.0 mL	10.0 mL	0 mL	0 mL

(ii) Ground State pKa: Absorption Spectra

1. You will obtain the ground state equilibrium constant for this acid dissociation by using absorption spectroscopy. Be sure to make a background correction using distilled water first. Then, using the very acidic solution where only the acid form of 2-naphthol is present and the very basic solution where only the conjugate base is present, take the absorption spectrum of both species. (Suggested range: 250-400 nm. You should see a peak at about 344 nm for the conjugate base form and a peak at about 326nm for the acid.) Print both spectra and note the absorption maximum.

2. From the spectra taken in 1, you'll note that there is a region where the base is the only form to absorb. Pick a wavelength in this region. You will use the absorbance of the pure conjugate base solutions at this wavelength to find the proportionality constant between absorption and concentration for the base form. Look up Beer's law for your pre-lab to see how the absorption is related to the concentration.

3. Take the absorption spectra of the three buffered solutions. Print out a plot with all 5 spectra overlayed. What trends do you see? If you have made your solutions consistently, all the spectra should intersect at a single point, the isostilbic point. Be sure to label the spectra. Also, note the absorption of all your solutions at the wavelength chosen in step 2. From the absorption at these wavelengths and the proportionality constant found in step 2, you can find the concentration of the base form of 2-naphthol for each of the solutions. Since you know the total concentration of 2-naphthol in all forms and the concentration of 2-naphthol in base form, you can find out the concentration of 2-naphthol in the acid form.

4. Plot pH versus $\log \frac{[NO^-]}{[NOH]}$ and do a least squares fit to your data using your favorite program. What's the ground state equilibrium constant? How does it compare with the literature value for the pKa of 2-naphthol?

5. Use the absorption maxima for the acid and base forms of 2-naphthol to estimate the excited state equilibrium constant. How does it compare with the literature value?

(iii) First Excited State pKa:* Fluorescence Spectra

1. Take the fluorescence emission spectra of the pure acid and pure base forms.
a. To do this, you will need to excite the acid at the frequency of its absorption maximum, 326nm. Then, scan the emission in the range 336-500nm. Save this spectrum. Now, take an excitation spectrum. In this case, you will watch the emission at the fluorescence maximum (354nm), and do an excitation scan from 300-344nm. This gives you a profile of the absorption on the same instrument as the emission. This avoids rescaling to compensate for different instrument signals. Overlay the emission and excitation spectra and find the frequency of the crossing point. It should be between 330 and 340 nm. This is the 0-0 frequency for the acid.
b. Now you can take the same spectra for the base form. However, the base should be excited at its absorption maximum, 344nm. The scan of the emission should have a range of 354-500nm. When taking the excitation spectrum, you should watch the emission at the emission maximum which is around 419nm. The excitation range can be 300-409nm. Again overlay the emission and excitation spectra. The 0-0 frequency should be between 370 and 380 nm.
2. Now take the emission spectra of your intermediate pH solutions and overlay them.

What pattern do you see? If you've made your solutions consistently, the spectra should intersect at a single point, the isostilbic point.

3. Now, use this 0-0 frequency to predict the excited state pKa*. How does it compare with the literature value? How does it compare with the pka* obtained using the absorption maxima and fluorescence maxima?

B. Protonation and Deprotonation Rate Constants for the First Excited State

1. Make the following solutions in 25.0 mL volumetrics.

Solutions	1.00×10^{-3} M 2-Naphthol	0.50 M H_2SO_4	0.200 M NH_4Ac	0.50 M NaOH
1	2.00 mL	5.0 mL	0.0 mL	0.0 mL
2	2.00 mL	0.0 mL	2.0 mL	0.0 mL
3	2.00 mL	0.0 mL	4.00 mL	0.0 mL
4	2.00 mL	0.0 mL	6.00 mL	0.0 mL
5	2.00 mL	0.0 mL	10.00 mL	0.0 mL
6	2.00 mL	0.0 mL	16.00 mL	0.0 mL
7	2.00 mL	0.0 mL	0.0 mL	5.00 mL

2. Obtain the emission spectra of all your solutions exciting at 320nm. Recond the emission spectra in the range 336-500nm. Overlay the spectra and record the emission at the emission maximum for 2-naphthol (~354nm). You can locate the maximum with the acid solution and use that as the monitoring wavelength in all your solutions. Record the intensity at this wavelength for all your solutions.

3. Obtain the sum of the fluorescence and nonradiative decay constants by analysing the fluorescence lifetime data for 2-naphthol in 0.10 M sulfuric acid. We don't have an instrument fast enough to measure this so you'll use the data of Boyer et al. which is listed below. Use your favorite program.

Time (ns)	Intensity (photons emitted/time)
0.0	21753
1.0	18907
2.0	16380
3.0	14171
4.0	12432
5.0	10757
6.0	9288
7.0	8138
8.0	7083
9.0	6014
10.0	5350

4. Plot $\frac{I_0}{I}$ as a function of the acetate concentration. From this plot, obtain k_d^* and $k_{Ac^-}^*$. Find k_p^*. Rember I_0 is the intensity of the pure acid solution. Your plot should include solutions 2-6.

C. Electron density near oxygen

Use Gaussian to obtain the HOMO and LUMO for 2-naphthol with the PM3 method. Refer to the instructions given in the introduction to using Gaussian. This time instead of simply submitting the job after choosing Opt+Freq, choose an empty basis set and then add the word PM3 in the key word section. PM3 is a semi-empirical method which is sufficient for our purposes and takes less time that the ab initio methods. PM3 only considers valence electrons. You'll need to keep this in mind when selecting the HOMO and LUMO. Then, do the same analysis you did in the tutorial with formaldehyde.

Promoting an electron from the HOMO to the LUMO changes the electron density. The change in electron density is reflected in the change you see between the HOMO and the LUMO. Notice what happens. Make sure to discuss this in relation to your values for the equilibrium constants for the ground and excited states.

Group Strategy: Each group should do 1-4 the first week and 5-8 the second week.

Events	Group 1	Group 2	Group 3
A(i) Preparing Solutions	1	1	1
A(ii) Ground State pka: Absorption spectra and analysis.	2	4	3
A (iii), First Excited State pka*: Fluorescense Spectra	3	2	4
B 1. Preparing solutions	5	5	5
B 2 Emission Spectra	7	7	6
B 3 Getting the sum of the fluorescence and nonradiate decay constants	4	3	2
B 4 Analysis of Emission Spectra	8	8	7
C Electron Density	6	6	8

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C. Marzzacco and L. Cooley, "The ground and Excited State Ionization Constants of 2-Naphthol", " The Rate Constants for the Excited-State Deprotonation-Protonatonation Reaction of 2-Naphthol."

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1999

EXHIBIT D

INTERNATIONAL MEETING

- **XIXth International Conference on Photochemisty** (ORAL PRESENTATION)

"SINGLE AND MULTI-PHOTON REACTIONS OF HOT MOLECULES"

Tomoyuki YATSUHASHI, Nobuaki NAKASHMA

(Duke Univ. NC USA, Aug01-06)

Hot molecule, which is in a highly vibrationally excited state, plays an important role in VUV-UV photochemistry. Hot molecules have a very high equivalent vibrational temperature of around 2000-4000K, and a narrow initial energy distribution which are suitable for examining the dynamics of high temperature chemistry. We have investigated several photochemical reactions of hot molecules in the gas phase with VUV lasers. Some examples of hot molecule reactions will be presented with respect to single and multi-photon reactions. 1) Benzyne has been known as a very important intermediate in organic synthesis processes. VUV laser irradiation of phthalic anhydride resulted in the formation of benzyne via hot phthalic anhydride. 2) Coumarin derivatives are known as useful laser dyes, however, unsubstituted coumarin emits little fluorescence. The two-photon decarbonylation reaction of coumarin was observed with a VUV laser. The triplet state of coumarin did not participate in the decomposition reaction. The hot coumarin acted as an intermediate in the multiphoton reaction. The subsequent second photon absorption by hot coumarin would be necessary to overcome the activation energy of the decomposition reaction. New photochemical reactions are expected for the hot molecule as an intermediate in multiphoton reactions.

A summary of recent hot molecule chemistry in our laboratory.

DOMESTIC MEETINGS

- **Bunsikouzou Sougou Touronkai** (Poster)

"Multiphoton dissociation of 2,2,2-paracyclophane by hot molecule mechanism"

Tomoyuki Yatsuhashi, Ken Ohtakeyama, Yuriko Hosoi, Seiji Shimizu, Nobuaki Nakashima

(Osaka Univ. Sep27-30)

Photodissociation of gaseous 2,2,2-paracyclophane (3PCP) was observed by an ArF laser excitation. The formation of p-quinodimethane was clearly observed as in the case of 2,2-paracyclophane (2PCP). The difference in the photolysis of those compound was found in the transient absorption spectra. The precursor radical may be observed in the case of 3PCP due to the relatively low vibrational temperature than 2PCP. The RRKM calculation and foreign gas pressure effect revealed that the dissociation of 3PCP was taken place with three photon process. The hot molecule mechanism was found valid even in the case of 3PCP which is the largest molecule ever examined.